

(12)

# EUROPEAN PATENT APPLICATION

(21) Application number: 86309316.7

(51) Int. Cl.<sup>3</sup>: B 32 B 27/32  
C 08 L 23/10

(22) Date of filing: 28.11.86

(20) Priority: 29.11.85 US 803029

(43) Date of publication of application:  
22.07.87 Bulletin 87/30

(64) Designated Contracting States:  
AT BE CH DE ES FR GB GR IT LI LU NL SE

(71) Applicant: AMERICAN CAN PACKAGING INC.  
American Lane P.O. Box 2600  
Greenwich Connecticut 06836-2600(US)

(72) Inventor: Genaka, Roger Peter  
971 Nanning Road  
Neenah Wisconsin 54956(US)

(74) Representative: Harvey, David Gareth et al.  
Graham Watt & Co. Riverhead  
Sevenoaks Kent TN13 2BN(GB)

(54) Polymeric films and processes for making them, multiple layer polymeric films and packages made from the films.

(57) Polymeric film and multiple layer sheet structure consist of and include, respectively, a layer made from a blend of polyisobutylene and a polypropylene copolymer, the latter including 2 - 30 mole percent ethylene moieties and the blend layer containing at least 1.8 mole percent ethylene. Plural layer structures can have two, three or more layers, e.g. five to seven layers. One such structure comprises the following layers, taken in order: blend layer (12) - adhesive layer (16) - primer layer (18) - metal foil layer (14) - adhesive layer (20) - abuse resistant layer (22). This structure is useful for packaging oxidisable products, for the foil layer (14) is a barrier to gas transmission through the structure, and the blend layer is capable of forming heat seals useful in making an hermetically-closed package.

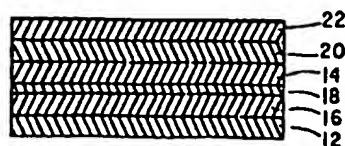


FIG. 4

"POLYMERIC FILMS AND PROCESSES FOR MAKING THEM,  
MULTIPLE LAYER POLYMERIC FILMS AND PACKAGES MADE  
FROM THE FILMS"

This invention pertains to packaging and more  
5 particularly to polymeric films and processes for  
making them, multiple layer polymeric films and  
packages made from the films.

This invention pertains in some respects to  
compositions of matter and single layer polymeric  
10 films made therefrom, and in other respects to multiple  
layer sheet materials and packages made therefrom.  
The sheet materials may be entirely polymeric, or  
they may include non-polymeric components such as  
metal or paper layers. The multiple layer materials  
15 may be flexible, or relatively rigid. The invention  
also pertains to processes for making the sheet  
materials. This invention is especially concerned  
with sheet materials for packaging, which are formed  
into packages e.g. by heat sealing.

20 Various packaging applications, wherein a  
product is packaged in heat sealable sheet material,  
require that the finished package be able to withstand  
substantial abuse, such as in shipping and handling.  
In some packaging applications, the package, i.e.  
25 the packaging materials and the product being packaged,

may have to be subjected to certain process treatments either during or after filling and sealing of the packag . One instance is a retortable package, where the package is subjected to sterilizing conditions typically involving a temperature about 250°F (121°C) and appropriate pressures for steam sterilization, typically for periods of 30 - 60 minutes, but sometimes as little as 10 minutes is acceptable.

A multiplicity of packaging materials have been developed for use in heat seal-type packaging. While many of these packaging materials have experienced a degree of success, problems remain with packages which are subject to certain abuses related to their use. More particularly, packages containing liquid products experience hydraulic pressures exerted by the liquid product when they receive physical shocks such as when dropped, or moved in a rough manner. Where the shock is sufficiently strong, the heat seals may break. While certain sheet structures are being used, it would be desirable to develop improved economical sheet structures which can be used to make even stronger packages, and particularly, stronger package sealant layers and seals, to reduce the incidence of failure of the filled and sealed package. Packaging materials which have been subjected

to high temperature processing are particularly susceptible to failure of the package seals especially when the package is abused.

Particularly referring, now, to packages which  
5 are subjected to thermal processing, as in retort processing typically at about 250°F( 121°C), sealant layers are known to be made of polypropylene, as in US-A-4,190,477. While polypropylene sealant layers are functionally capable of withstanding  
10 the processing conditions, the heat seals, as measured after processing, could desirably be stronger.

It is an object of this invention to provide improved packaging sheet materials, for example having improved capability to withstand physical  
15 shocks when formed into flexible heat sealed packages filled with liquid, improved packages made from these sheet materials, and processes of making such sheet materials.

Desirably, some such sheet materials will  
20 have good barrier properties to prevent or minimise transmission of gases or moisture into or out of the package.

Apart from seeking sheet materials capable of withstanding substantial physical shocks when  
25 formed into flexible heat sealed packages .led

with liquid, and of providing a good barrier to transmission of gases or moisture, we have sought to develop sheet materials having sufficient optical clarity to enable visual inspection of the contents of and packages made from those sheet materials.

According to the present invention, there is provided a polymeric film made from a blend of 10% to 65% by weight polyisobutylene and 90% to 35% by weight polypropylene copolymer, the polypropylene copolymer comprising 70 to 98 mole percent propylene moieties and 30 to 2 mole percent ethylene moieties, and the overall composition of the blend comprising at least about 1.8 mole percent ethylene.

Also according to this invention, there is provided a multiple layer sheet material, comprising:

(a) a first polypropylene-based layer which is a blend of 35% to 90% by weight polypropylene copolymer and 65% to 10% by weight polyisobutylene, the polypropylene copolymer comprising 70 to 98 mole percent propylene moieties and 30 to 2 mole percent ethylene moieties, the overall composition of said blend comprising at least about 1.8 mole percent ethylene; and

(b) a second layer comprising a metal foil affixed on one surface of the first layer.

According to another aspect of the invention,  
there is provided a process for making polymeric  
film, the process comprising the steps of:

(a) forming a particulate blend comprising  
5 polypropylene copolymer and polyisobutylene, the  
particles in said blend generally having a size  
greater than 0.5 micron diameter;

(b) extruding the blend through a slot die;  
and

10 (c) cooling the extruded blend to form a solid  
film.


Another process according to the invention  
is for making a multiple layer film, the process  
comprising the steps of:

15 (a) forming a particulate blend comprising  
polypropylene copolymer and polyisobutylene; and

(b) coextruding the blend with a polyamide  
and a polymeric barrier material to form a multiple  
layer sheet material,

20 said sheet material comprising, in order through  
the sheet material, a first layer comprising the  
blend, a second layer of a polyamide, a third layer  
of barrier material and a fourth layer of a polyamide,  
the barrier material for example including or consisting  
25 of ethylene vinyl alcohol copolymer.

One multiple layer film embodying the invention



comprises:

(a) a first polypropylene-based layer which is a blend of 35% to 90% by weight polypropylene copolymer and 65% to 10% by weight polyisobutylene, the polypropylene copolymer comprising 70 to 98 mole percent propylene moieties and 30 to 2 mole percent ethylene moieties, and the overall composition of said blend comprising at least about 1.8 mole percent ethylene;

(b) a second layer of a polyamide, having one of its surfaces adhered to one surface of the first layer;

(c) a third, barrier layer having one of its surfaces adhered to the other surface of the second polyamide layer the composition of the third layer comprising (i) about 50% to about 90% by weight ethylene vinyl alcohol copolymer and (ii) about 50% to about 10% by weight of a polymer compatible with ethylene vinyl alcohol copolymer in blend composition, which polymer, for example, is polyetheramide block copolymer; and

(d) a fourth layer of a polyamide, having one of its surfaces adhered to the other surface of the third layer.

Another multiple layer film embodying the

invention comprises:

(a) a first, polypropylene-based layer which is a blend of 35% to 90% by weight polypropylene copolymer and 65% to 10% by weight polyisobutylene, 5 the polypropylene copolymer comprising 70 to 98 mole percent propylene moieties and 30 to 2 mole percent ethylene moieties, and the overall composition of the blend comprising at least 1.8 mole percent ethylene; and

10 (b) a second layer of a vinylidene chloride copolymer, which is adhered to one surface of the first layer by an intervening third layer of adhesive.

The invention comprehends packages made from polymeric films and sheet materials as defined above, 15 such packages for example being fabricated from confronting plies of film or sheet material which are heat sealed around their borders.

The invention will be further explained in the non-limiting description which now follows.

20 The invention is embodied in one aspect in an unsupported polymeric film which is a blend of about 10% to 65% by weight polyisobutylene and conversely about 90% to 35% by weight of polypropylene copolymer. The polypropylene is preferably a copolymer 25 having about 70 to about 98 mole percent propylene



moieties and conversely about 30 to about 2 mole percent ethylene moieties. Preferred films have a blend composition of 20% to 40% by weight polyisobutylene and 80% to 60% by weight polypropylene copolymer. It is also preferred that the polypropylene copolymer is 92 to 98 mole percent propylene moieties and conversely 2 to 8 mole percent ethylene moieties.

The preferred process of making the films includes the steps of extruding the blend through a die, and cooling the extruded blend to form a solid. In the process, it is entirely acceptable and in some cases preferred to form a particulate blend of the polypropylene copolymer and the polyisobutylene, wherein the particles in the blend generally have a size greater than 0.5 micron diameter. The blend can be coextruded with other polymeric materials to form plural layer sheet structures.


The invention is also embodied in multiple layer sheet materials. In one such sheet material, a first layer is polypropylene-based and is composed of a polypropylene blend of the invention. The polypropylene used in the blend may be a copolymer having 70 to 98 mole percent propylene moieties and conversely 30 to 2 mole percent ethylene moieties. A second layer of a metal foil is affixed on one

of the surfaces of the first layer. The first layer is preferably 60% to 80% by weight polypropylene copolymer and 40% to 20% by weight polyisobutylene.

In more preferred forms, the polypropylene copolymer  
5 in the first layer is 92 to 98 mole percent propylene moieties and 2 to 8 mole percent ethylene moieties.

In some embodiments of these sheet materials, the first layer is adhered to the second layer by an intervening polymeric adhesive. Other embodiments  
10 of the invention have additional layers. In one such embodiment, an abuse resistant layer is adhered to the other surface of the second layer (i.e. the metal foil layer) by an adhesive layer. Exemplary materials for use as the abuse resistant layer are  
15 oriented polyamides, oriented polyesters and oriented polypropylenes.

In one family of embodiments, the invention is exemplified by a multiple layer sheet material having a first layer of the blend of polypropylene  
20 copolymer and polyisobutylene and a second layer of metal foil, and then it may be convenient to adhere the first layer to the second layer by use of an intervening adhesive layer of polypropylene copolymer. In some cases, it is expedient to include  
25 a primer between the second layer and the polypropylene copolymer layer. A preferred primer has carboxy



moieties. Further, the layer of polypropylene copolymer includes carboxy moieties in some embodiments.

In another family of embodiments, the invention is exemplified by a multiple layer sheet material having barrier properties provided by certain polymeric materials. A first layer is of the blend of polypropylene copolymer and polyisobutylene. A second layer of a polyamide has one of its two opposing surfaces adhered to one surface of the first layer.

10 A third barrier layer has one of its two opposing surfaces adhered to the other surface of the polyamide second layer. A preferred composition for the third layer is about 50% to about 90% by weight of a first material which is vinyl alcohol copolymer and about

15 50% to about 10% by weight of a second material which is a polymer compatible with ethylene vinyl alcohol copolymer in blend composition. "Compatible" means the capability for polymers to be extruded in blend composition. A fourth layer of the structure

20 is a polyamide, which has one of its two opposing surfaces adhered to the other surface of the third layer. In some preferred versions of this family of embodiments, the second material is polyetheramide block copolymer. For structures desiring or requiring

25 higher levels of adhesion, a layer of an adhesive

polymer may be interposed between the first and second layers. Finally, a fifth layer of biaxially oriented nylon may be adhered to the other surface of the fourth layer.

5           Within the family of embodiments having barrier properties provided by polymeric materials, one sub-family uses as the barrier layer a second layer comprised of vinylidene chloride copolymer. The second layer is adhered to the first layer on one  
10 of its surfaces by a third layer of an adhesive therebetween. A fourth layer of a polyamide may be adhered to the other surface of the second layer by a fifth layer of an adhesive therebetween.

          The various films and sheet materials of the  
15 invention are susceptible to being made into packages by the formation of seals defining enclosed areas, to effect the closing and sealing of the packages.

          Embodiments of the invention will now be described in more detail by way of example only with reference  
20 to the accompanying drawings, in which:

          FIGURE 1 is a cross-section through a single layer film embodying this invention,

          FIGURE 2 is a cross-section through a two-layer sheet material embodying the invention, which  
25 incorporates a metal foil layer,

FIGURE 3 is a cross-section through a three-layer sheet material embodying the invention, which also incorporates a metal foil layer,

5      FIGURE 4 is a cross section through a six-layer sheet material embodying the invention, which also incorporates a metal foil layer,

FIGURE 5 is a cross-section through a seven-layer sheet material embodying the invention, and

10      FIGURE 6 is a cross-section through a five-layer sheet material embodying the invention.

The invention is first seen in a single layer 12 of film of generally indefinite length. A cross-section of a piece of such a film is seen in FIGURE 1. The film is a blend of about 10% by weight to about 65% by weight polyisobutylene and about 90% to about 35% by weight polypropylene copolymer. The polypropylene copolymer is especially selected to contain about 70 to about 98 mole percent propylene moieties and about 30 to about 2 mole percent ethylene moieties. 15  
20      The overall blend composition has at least about 1.8 mole percent ethylene.

FIGURES 2 and 3 show the invention as it is embodied in a simple multiple or plural layer sheet structure wherein a layer of metal foil is joined 25  
to the blend layer. In the structure of FIGURE 2,

the foil layer 14 is adhered directly to the blend layer 12 without the use of intervening adhesives.

The structure of FIGURE 3 is similar but has a third, adhesive layer 16 to promote improved adhesion between  
5 layers 12 and 14.

FIGURE 4 illustrates a more complex form of sheet structure embodying the invention, which includes therein a layer of metal foil. The FIGURE 4 structure includes the same layers 12, 14, and 16 as in FIGURE 3,  
10 but in addition has an optional primer layer 18 between layers 14 and 16. An abuse resistant layer 22 is adhered to foil layer 14 by an intervening adhesive layer 20.

FIGURE 5 illustrates a multiple layer polymeric  
15 barrier film according to the invention. In this embodiment, an adhesive layer 30 is adhering a nylon layer 24 to the blend layer 12. A barrier layer 26 includes ethylene vinyl alcohol copolymer (EVOH) for reducing transmission of gases through the film.  
20 Nylon layer 28 is adjacent EVOH layer 26. An abuse resistant layer 22 is shown adhered to nylon layer 28 for the purpose of providing further physical protection of the overall film, but this layer 22 is optional.

25 FIGURE 6 shows another embodiment of a multiple

layer barrier film which uses, as a barrier, a layer  
34 of vinylidene chloride copolymer. In this  
illustrated embodiment, layer 12 is the blend layer,  
layer 36 is a barrier layer of Saran<sup>®</sup> and layer  
5 40 is a layer of nylon. Intervening layers 34 and  
38 are adhesives functional to hold the respective  
layers to each other, and functional to hold the  
structure together as a whole.

It is entirely possible to incorporate the  
10 invention, including any of the embodiments herein,  
as a substructure, into other structures. Similarly,  
additional layers may be added to any of the structures  
specifically disclosed herein without departing  
from the scope and intent of the invention.

15 THE BLENDS

The blends of layer 12 have two essential  
components. The first component is polyisobutylene.  
The second component is polypropylene copolymer.  
We have found that it is critical that the poly-  
20 propylene component contain some ethylene in order  
to impart to the overall blend composition the desired  
degree of shock resistance. The polypropylene  
component of the blend may be all copolymer or a  
blend of copolymer and homopolymer. The recitation  
25 of polypropylene copolymer hereinafter includes

blends of copolymer and polypropylene homopolymer.

While blends of polypropylene and polyisobutylene may be made using polypropylene homopolymer, and heat sealable sheet materials may be made therefrom, those sheet materials exhibit less shock resistance than the preferred structures of the invention.

With the inclusion of as little as about 1.8 mole percent ethylene in the propylene component, improvement is seen in the shock resistance of packages made therefrom. As the amount of ethylene is increased, the shock resistance generally improves, and up to about 30 mole percent ethylene may be used.

As the amount of ethylene is increased, the capability of the blend to withstand heat (heat resistance) is decreased. At the higher fractions of ethylene content, the heat resistance is less than desired for some uses. Thus, for those uses in which the packaging sheet material is required to have high heat resistance, an ethylene content of about 2 to about 8 mole percent is preferred in the polypropylene copolymer, and the presence of at least about 2 mole percent is necessary as a condition in this invention.

Since the various polymeric layers in the invention are intended to be used primarily in extrusion



process through a slot die, it is significant that each material be obtained in such a form as is readily conducive to its use in the extrusion process, and that it be obtained at economically favorable cost.

5 As is well known, polyisobutylene is commercially supplied in the form of large blocks, or bales. In order to prepare polyisobutylene for extrusion, it is thus necessary to convert it to another form. Conversion of polyisobutylene into pellets is not  
10 known to have been done. Its rubbery physical characteristics may prevent its being prepared in pellet form, as is, for example, the polypropylene copolymer. The polyisobutylene may be melted from the bale and blended with a polypropylene, either  
15 copolymer or homopolymer, to form a master batch of a blend of polyisobutylene and polypropylene. The so-formed master batch may be formed into conventional pellets for use in extruding the blends of this invention to form layers. In making the  
20 final blends for use herein, the master batch pellets may be blended with additional polypropylene, which must include copolymer, to make the desired blend ratio of polyisobutylene to polypropylene.

The preparation of a master batch by melt  
25 mixing together polyisobutylene with polypropylene

copolymer to form a blend is seen as significant to the desired objective of economically forming a film from a blend of polyisobutylene and polypropylene copolymer. While a master batch may be so blended as to yield a blend composition as desired for forming a film, it is usually preferred to form a master batch having a lower polypropylene content and to form it into conventional pellets suitable for extrusion. This minimizes both the cost of making the master batch and the thermal exposure of the polypropylene. The final desired blend composition is economically achieved by dry blending a pre-determined amount of the master batch pellets with a pre-determined amount of polypropylene copolymer pellets and extruding the mixture, thus achieving the desired final blend composition in the extruded layer.

In a typical formation of blend layers in practising the invention, a master batch is compounded by melting polyisobutylene and mixing into the melt an amount of polypropylene, preferably as pellets, sufficient to make a blend of 65% by weight polyisobutylene and 35% polypropylene. The blend is heated sufficiently to melt all the polypropylene, and is mixed thoroughly. The melted master batch blend is then formed into pellets and cooled. In the

formation of the final composition, pellets of the master batch are mixed with pellets of a selected polypropylene copolymer. A typical blend ratio with the above-mentioned master batch is 42% by weight polypropylene copolymer and 58% by weight master batch. The final composition is thus 37.7% polyisobutylene and 62.3% polypropylene, including the polypropylene in the master batch. Where the selected polypropylene copolymer is, for example 4% ethylene, and it is used for both the blend component and in the master batch, the overall content of the blend is 2.5% ethylene.

The blends used in the invention may be compounded in the melted mixture of the master batch in the desired final blend ratio to be extruded. When the desired final blend is thus made as the master batch, the compounded pellets may be extruded without further addition, as of pellets of polypropylene copolymer. While this process, which eliminates a step of dry blending, does produce acceptable blends for use in the invention, where the at least 1.8 percent ethylene is present in the form of polypropylene copolymer, the cost of processing the additional polypropylene in the melt compounding operation usually exceeds the cost of the eliminated

dry blending step. Thus, the two step process is usually preferred in preparing material for extrusion processing.

#### THE MULTIPLE LAYER MATERIALS

5       The blends described above have preferred utility when used with additional layers. The additional layers may be polymeric or non-polymeric. Conventional additives and fillers may be used. Normal amounts of additives and modifiers may be  
10       included in the blend layer 12.

      In the formation of the sheet material of FIGURE 2, it is desirable to select, for inclusion in the blend composition of layer 12, a polymer having carboxy modifications thereto, to enhance  
15       adhesion between blend layer 12 and metal foil layer 14. Carboxy modified propylene polymers are available from Mitsui Company, Japan as "QF" series polymers.

      Another way of obtaining adhesion between layers 12 and 14 is through a separate layer of  
20       adhesive as at 16 of FIGURE 3. A relatively thin layer of adhesive may be used, such as 2 to 3 pounds per 3000 square foot ream ( $3.2$  to  $4.9 \times 10^{-3}$  kg/m). Various adhesives are conventionally known for use in adhesion to metal foil, as in layer 14. Exemplary  
25       of these adhesives, for use in layer 16 are the

curing type polyester urethane adhesives. One such acceptable adhesive is available from Morton Chemical Company as Adcote 506-40. The adhesive layer 16 may be in direct contact with the foil layer 14, or a primer layer, as at 18 in FIGURE 4 may be interposed between foil layer 14 and adhesive layer 16. The primer layer 18, when used, is only of sufficient thickness to ensure its continuity. A suitable primer is Morprime from Morton Chemical Company, a modified polypropylene provided in a liquid carrier. The liquid primer is conveniently applied to the surface of the metal foil layer 14, and the liquid removed by evaporation.

The primer may then be cured by application of heat. Finally, the adhesive layer 16 and blend layer 12 are applied to the primed foil layer 14, preferably with pressure to promote adhesion between the several and respective layers in the composite structure of layers 12, 14, 16 and 18.

In completion of the structure shown in FIGURE 4 an abuse resistant layer 22 may be adhered to the other surface of foil layer 14 by use of an adhesive layer 20. Materials conventionally known for their abuse resistance properties, such as oriented nylon, oriented polyester and oriented polypropylene, are

satisfactory. Conventional adhesives are known for adhering the abuse resistant materials to metal foil. The adhesive selected will, of course, depend on the selection of the abuse resistant layer.

5 In one such combination, a layer 22 of biaxially oriented nylon is adhered to foil layer 14 by a curing-type polyester urethane adhesive.

The metal foil layer 14 in the embodiments of FIGURES 2, 3 and 4 provides an excellent barrier  
10 to transmissions of gases and light through the sheet structure. There are, however, applications for sheet materials where the use of the metal foil is not desirable. FIGURES 5 and 6 illustrate multiple layer films having polymeric layers that provide  
15 barriers to gaseous transmissions through the films.

In the structures of FIGURE 5, layer 12 is the polyisobutylene-polypropylene copolymer blend. Layers 24 and 28 are nylon. Layer 26 is EVOH or a blend of EVOH. Layer 30 is an adhesive effective  
20 to bond layers 12 and 24 into the structure. Layer 22 is an abuse resistant layer, adhered to nylon layer 28, optionally through use of an adhesive layer 32. Layers 24 and 28 preferably contain nylon  
6 and may contain other polyamide polymers. Other  
25 nylons may be substituted for nylon 6 where heat

resistance is not critical. While layers 26 may be EVOH, a preferred composition for layer 26 is a blend of 50% by weight to 90% by weight of a first polymer of EVOH and 50% by weight to 10% by weight of a second polymer compatible with EVOH in blend composition. The second polymer may be selected with a substantial degree of freedom, and initial determination of suitability of any given polymer is dependent primarily on its compatibility in blend composition with EVOH. Among the suitable choices for the second polymer are ethylene ethyl acrylate, ethylene acrylic acid, linear low density polyethylene, ionomer, anhydride modified low density polyethylene, anhydride modified medium density polyethylene, anhydride modified high density polyethylene, nylon, and polyetheramide block copolymer. The selection of the specific material for the second polymer will, of course, depend on the composition and use of the overall multiple layer structure. With the disclosure herein, expedient selection of the second polymer can be made by those of average skill in the art.

Adhesive layers 30 and 32 may conveniently be polyester urethane, and the structure may conveniently be formed by adhesive lamination techniques.

In formation by adhesive lamination, three separate substructures may initially be formed. The first substructure is the blend layer 12 which is formed by extrusion as for the single layer film of FIGURE 1.

5 The second substructure is the three layer substructure /nylon/EVOH/nylon/ of layers 24, 26 and 28. This three layer substructure is conveniently formed by conventional coextrusion. The third substructure is the abuse resistant layer 22, which is typically  
10 formed by conventional extrusion and which is usually followed by molecular orientation. After the three substructures are formed, they may be combined by conventional lamination processes. They may alternatively be combined by other processes such  
15 as extrusion lamination processes.

In another process for making multiple layer films as in FIGURE 5, layers 12, 30, 24, 26 and 28 may be coextruded as a first substructure. Layer 22 is separately prepared as above. Layer 22 is  
20 joined to layer 28 by conventional methods.

Another family of multiple layer structures of the invention is illustrated in FIGURE 6. Layer 12 is the blend layer. Layer 36 is a vinylidene chloride copolymer. Preferred copolymers for layer  
25 36 are vinyl chloride-vinylidene chloride copolymers



and vinylidene chlorid methacrylate copolymers.

Layer 40 is nylon. Layers 34 and 38 are adhesives which adhere together the several layers of the structure. The structure is typically formed by separately forming layers 12, 36 and 40 by individual extrusion processes. The composite multiple layer structure is then assembled by conventional combining process, such as adhesive lamination, extrusion lamination or the like.

Other combinations of conventional processes can be used to form the structures of the invention, and will now be obvious to those skilled in the art.

Sheet materials such as those illustrated in FIGURES 5 and 6 may be formed from materials, each of which offers substantial optical transparency. The finished sheet materials represented by FIGURES 5 and 6 also typically have sufficient optical clarity through the sheet material to enable visual inspection of the package contents. Other structures of the invention which do not use opaque materials such as metal foil, paper or fillers, also typically offer the same optical clarity.

Flexible packages, of the pouch type, may be made from any of the single or multiple layer

sheet materials of the invention using conventional processes to form heat seals about an enclosed area defined by facing portions of the sheet material.

The sheet materials may also be used in combination with other packaging structures. Sheet structures may, for example, be used as lid materials for rigid trays formed from other packaging structures.

The invention will now be illustrated further by the following non-limiting Examples.

10

EXAMPLE 1

Pellets of polypropylene copolymer, containing 4% ethylene were mixed with pellets of a master batch which consisted of 65% polyisobutylene and 35% polypropylene copolymer, where the polypropylene copolymer used in the master batch contained 4% ethylene. The mixture was 58% by weight pellets of the master batch and 42% pellets of the polypropylene copolymer yielding a blend which was 37.7% polyisobutylene, 59.8% propylene and 2.5% ethylene. The mixture was extruded through a slot die to form a single layer film 4 mils (0.10 mm) thick. The so-prepared film was laminated to one surface of a layer of 35 gauge aluminum foil using a polyester urethane adhesive. The other surface of the foil was laminated to a layer of 60 gauge biaxially oriented

nylon, using a polyester urethane adhesive.

#### EXAMPLE 2

A sheet structure was prepared as in EXAMPLE 1 except that the polypropylene used to make the master batch was a homopolymer.

#### COMPARATIVE EXAMPLE 1

A sheet structure was prepared as in EXAMPLE 1 except that the layer comparable to the blend layer in EXAMPLE 1 was polypropylene copolymer, without any polyisobutylene.

#### COMPARATIVE EXAMPLE 2

A sheet structure was prepared as in EXAMPLE 2 except that the polypropylene blended with the master batch was a homopolymer.

#### EXAMPLE 3

A single layer film was prepared for the blend layer as in EXAMPLE 1. A three-layer substructure was prepared by coextruding an EVOH layer as a core layer with outer layers of nylon, to form a substructure of the nature of /nylon/EVOH/nylon/. The three-layer substructure was then laminated to the blend layer using a polyester urethane adhesive.

#### EXAMPLE 4

A five layer film was prepared by coextruding through a combining die a structure of

/nylon/EVOH/nylon/adhesive/blend/. The blend layer was the same mixture as was prepared by mixing pellets for extrusion in EXAMPLE 1. The adhesive material was QF500X, for Mitsui Company, Japan. In the finished film, the blend layer is 4.0 mils (0.10 mm) thick. The EVOH layer was 0.5 mil (0.013 mm) thick. The nylon layers are 0.25 mil ( $6.3 \times 10^{-3}$  mm) thick. The adhesive is minimal thickness for continuity, about 0.1 mil ( $2.5 \times 10^{-3}$  mm).

10                    EXAMPLE 5

A single layer film was prepared for the blend layer as in EXAMPLE 1. The blend layer was laminated to one surface of a layer of biaxially oriented Saran <sup>®</sup> using a polyester urethane adhesive having an aliphatic chain catalyst. A layer of 60 gauge biaxially oriented nylon was laminated to the other surface of the Saran <sup>®</sup> using the same polyester urethane adhesive.

EXAMPLE 6

20            A multiple layer sheet material was made as in EXAMPLE 1 except that the ratio of the mixture of pellets in the blend layer was 30% by weight pellets of the master batch and 70% pellets of the polypropylene copolymer. The resulting blend composition was 19.5% polyisobutylene and 80.5%

25

polypropylene copolymer.

The she t materials of EXAMPLE 1, EXAMPLE 2  
and Comparative Example 1 were used to make heat  
sealed packages containing about 100 fl. oz. (2.96 l)  
5 of water. The edge seals were 3/8 inch (9.5 mm)  
wide. The packages were then retort processed at  
250°F (121°C) and about 25 psig (1.72 bar) pressure  
for 30 minutes. The retort processed packages were  
cooled to room temperature. A test package was  
10 then placed in a simulated shipping container.  
A flat, uniform weight was placed on top of the  
package; a 14 lb. (6.36 kg) weight to simulate stacking  
the packages 3 high, or a 35 lb. (15.89 kg) weight  
to simulate stacking the packages 6 high.

15 The shipping containers were then dropped  
onto a hard surface from various heights at 6 inch  
(15.2 cm) intervals. Each package was subjected  
to one drop from a selected height. After the drop,  
each package was inspected for weakening or failure  
20 at the seal area. In general, six drops were made  
of six packages at each height reported. In some  
cases, the package seals were substantially weakened,  
as evidenced by stretching, or narrowing of the  
seal width though no leakage occurred. These weakened  
25 packages were counted as failures. The results



of all the tests are seen in Table 1.

TABLE 1

Sample Identification	Drop Height Survived Without Package Failure	
	14. lb. top load (6.36 kg)	35. lb. top load (15.89 kg)
Example 1	all survive at 24 inches (0.63 m)	all survive at 6 inches (15.2 cm)
Example 2	all survive at 18 inches (0.46 m)	all fail at 6 inches (15.2 cm)
Comparative Example 1	60% fail at 24 inches (0.63 m)	- - - - -
	all fail at 6 inches (15.2 cm)	all fail at 6 inches (15.2 cm)

The results show that the packages made from

15 the structures of EXAMPLE 1 and EXAMPLE 2 were

significantly better than the packages of Comparative

Example 1 wherein the blend layer did not contain

polyisobutylene. Further, packages of EXAMPLE 1

tended to be somewhat better than those of EXAMPLE 2

20 wherein the packages of EXAMPLE 2 contained more

homopolymer polypropylene component by virtue of

the homopolymer in the master batch.

Thus it is seen that the invention provides

novel sheet materials having improved capability

25 to withstand physical shocks when formed into flexible

heat sealed packages filled with liquid.

It is further seen that the sheet materials  
and packages embodying the invention provide good  
barrier properties to transmission of gases into  
5 or out of the package. Certain of the sheet materials  
and packages have good optical clarity through the  
sheet material, enabling visual inspection of the  
contents.

CLAIMS:

1. A polymeric film made from a blend of  
10% to 65% by weight polyisobutylene and 90% to  
35% by weight polypropylene copolymer, the polypropylene  
5 copolymer comprising 70 to 98 mole percent propylene  
moieties and 30 to 2 mole percent ethylene moieties,  
and the overall composition of the blend comprising  
at least about 1.8 mole percent ethylene.

2. A polymeric film according to claim 1,  
10 wherein the blend comprises 20% to 40% by weight  
polyisobutylene and 80% to 60% by weight polypropylene  
copolymer.

3. A polymeric film according to claim 1  
or claim 2, wherein said polypropylene copolymer  
15 comprises 92 to 98 mole percent propylene moieties  
and 2 to 8 mole percent ethylene moieties.

4. A polymeric film according to claim 1,  
2 or 3, made by the process of:

- (a) extruding the blend through a die; and
- 20 (b) cooling the extruded blend to form a solid.

5. A polymeric film according to claim 1,  
2 or 3, made by the process of:

- (a) forming a particulate blend comprising  
polypropylene copolymer and polyisobutylene, the  
25 particles in the blend generally having a size greater  
than 0.5 microns diameter;



(b) extruding the blend through a die; and

(c) cooling the extruded blend to form a solid.

6. A multiple layer sheet material, comprising:

(a) a first polypropylene-based layer (12)

5 which is a blend of 35% to 90% by weight polypropylene  
copolymer and 65% to 10% by weight polyisobutylene,  
the polypropylene copolymer comprising 70 to 98  
mole percent propylene moieties and 30 to 2 mole  
percent ethylene moieties, the overall composition  
10 of said blend comprising at least about 1.8 mole  
percent ethylene; and

(b) a second layer (14) comprising a metal  
foil affixed on one surface of the first layer.

7. A sheet material according to claim 6,  
15 wherein the first layer blend comprises 60% to 80%  
by weight polypropylene copolymer and 40% to 20%  
by weight polyisobutylene.

8. A sheet material according to claim 6  
or claim 7, wherein the polypropylene copolymer  
20 in the first layer blend comprises 92 to 98 mole  
percent propylene moieties and 2 to 8 mole percent  
ethylene moieties.

9. A sheet material according to claim 6,  
7 or 8, wherein the first layer (12) is adhered  
25 to the second layer (14) by an intervening

polymeric adhesive (16).

10. A sheet material according to claim 9,  
wherein a first surface of the second layer (14)  
is adhered by the polymeric adhesive (16) to one  
5 surface of the first layer (12), and wherein an  
abuse resistant layer (22) is adhered to the second  
surface of the metal foil second layer (14) by an  
adhesive layer (20).

11. A sheet material according to claim 10,  
10 wherein the abuse resistant layer (22) is biaxially  
oriented nylon.

12. A sheet material according to any of  
claims 6 to 11, wherein the first layer is adhered  
to a first surface of the second layer by a layer  
15 of polypropylene copolymer therebetween.

13. A sheet material according to claim 12,  
including a primer between the second layer and  
the polypropylene copolymer layer, the primer comprising  
carboxy moieties.

20 14. A sheet material according to claim 12  
or claim 13, wherein an abuse resistant layer is  
adhered to the opposite, second surface of the metal  
foil second layer, the abuse resistant layer for  
example being biaxially oriented nylon.

25 15. A sheet material according to any of

claims 12 to 14, wherein the layer of polypropylene copolymer includes carboxy moieties.

16. A multiple layer sheet material, comprising:

(a) a first polypropylene-based layer (12)

5 which is a blend of 35% to 90% by weight polypropylene copolymer and 65% to 10% by weight polyisobutylene, the polypropylene copolymer comprising 70 to 98 mole percent propylene moieties and 30 to 2 mole percent ethylene moieties, and the overall composition  
10 of said blend comprising at least about 1.8 mole percent ethylene;

(b) a second layer (24) of a polyamide, having one of its surfaces adhered to one surface of the first layer;

15 (c) a third, barrier layer (26) having one of its surfaces adhered to the other surface of the second polyamide layer (24) the composition of the third layer comprising (i) about 50% to about 90% by weight ethylene vinyl alcohol copolymer  
20 and (ii) about 50% to about 10% by weight of a polymer compatible with ethylene vinyl alcohol copolymer in blend composition, which polymer, for example, is polyetheramide block copolymer; and

(d) a fourth layer (28) of a polyamide, having  
25 one of its surfaces adhered to the other surface of the third layer (26).

17. A sheet material according to claim 16, wherein the blend of the first layer comprises 60% to 80% by weight polypropylene copolymer and 40% to 20% by weight polyisobutylene.

5        18. A sheet material according to claim 16 or claim 17, wherein the polypropylene copolymer in the first layer comprises 92 to 98 mole percent propylene moieties and conversely 2 to 8 mole percent ethylene moieties.

10       19. A sheet material according to claim 16, 17 or 18, further including a layer (30) of an adhesive polymer between said first and second layers (12, 14).

20. A sheet material according to any of claims 16 to 19, further including a fifth layer  
15 (22), of biaxially oriented nylon, on the other surface of the fourth layer.

21. A multiple layer sheet material, comprising:

(a) a first, polypropylene-based layer (12)  
which is a blend of 35% to 90% by weight polypropylene  
20 copolymer and 65% to 10% by weight polyisobutylene,  
the polypropylene copolymer comprising 70 to 98  
mole percent propylene moieties and 30 to 2 mole  
percent ethylene moieties, and the overall composition  
of the blend comprising at least 1.8 mole percent  
25 ethylene; and

(b) a second layer (36) of a vinylidene chloride copolymer, which is adhered to one surface of the first layer by an intervening third layer (34) of adhesive.

5           22. A sheet material according to claim 21, further including a fourth layer (40) of a polyamide adhered to the other said surface of the second layer by a fifth layer (38) of adhesive.

          23. A process for making a polymeric film,  
10 the process comprising the steps of:

(a) forming a particulate blend comprising polypropylene copolymer and polyisobutylene, the particles in said blend generally having a size greater than 0.5 micron diameter;

15           (b) extruding the blend through a slot die;  
and

(c) cooling the extruded blend to form a solid film.

          24. A process for making a multiple layer film,  
20 the process comprising the steps of:

(a) forming a particulate blend comprising polypropylene copolymer and polyisobutylene; and

(b) coextruding the blend with a polyamide and a polymeric barrier material to form a multiple  
25 layer sheet material,  
said sheet material comprising, in order through

the sheet material, a first layer comprising the blend, a second layer of a polyamide, a third layer of barrier material and a fourth layer of a polyamide, the barrier material for example including or consisting of ethylene vinyl alcohol copolymer.

25. A sheet material according to claim 24, wherein the barrier material comprises a blend of 50% by weight to 90% by weight ethylene vinyl alcohol copolymer and 50% by weight to 10% by weight of a polymer compatible with ethylene vinyl alcohol copolymer in blend composition.

26. A sheet material according to claim 24 or claim 25, wherein the blend is composed of particles which generally have a size greater than 0.5 micron in diameter.

27. A package made from the film product according to any of claims 1 to 5.

28. A package made from the sheet material according to any of claims 6 to 22.

29. A package made from film produced by the process according to any of claims 23 to 26.



FIG. 1

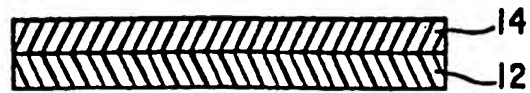


FIG. 2

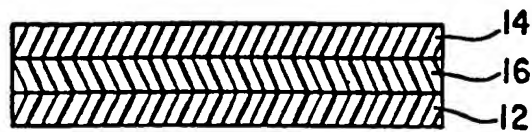


FIG. 3

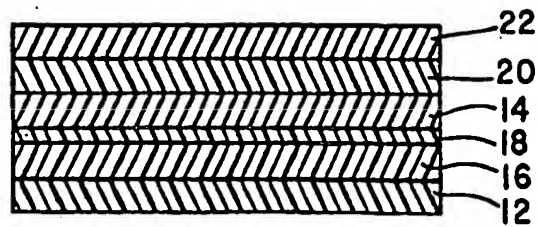


FIG. 4

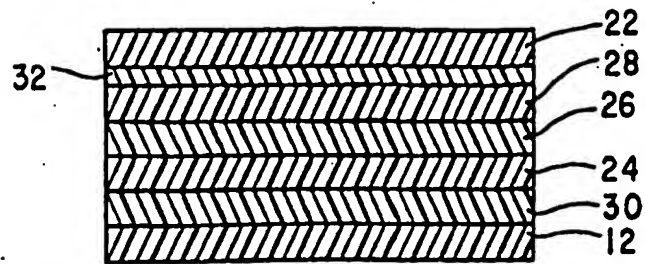


FIG. 5

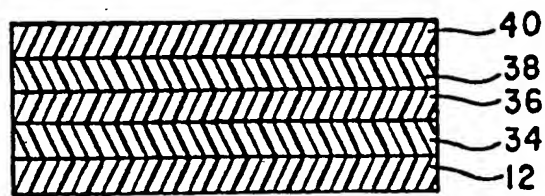


FIG. 6



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
A	GB-A-1 168 541 (CONTINENTAL CAN CO. INC) * Claims 1,5,6 *	1	B 32 B 27/32 C 08 L 23/10
			TECHNICAL FIELDS SEARCHED (Int. Cl. 4)
			B 32 B C 08 L
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 07-04-1987	Examiner VAN THIELEN J.B.
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons</p> <p>&amp; : member of the same patent family, corresponding document</p>			

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☒ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**